Volatile Contents in Vesicles in IDP Grains Analyzed with Scanning Transmission Electron Microscopy

Katherine D. Burgess[1], Rhonda M. Stroud[1], David Joswiack[2] and Donald Brownlee[2]

[1]*U.S. Naval Research Laboratory, Washington, DC*
[2]*University of Washington, Seattle, WA*

Chondritic porous interplanetary dust particles (IDPs) are believed to come from comets and incorporate a wide variety of primitive early solar system and interstellar materials. Alteration is thought to be from nebular processes, such as solar wind exposure, and atmospheric entry heating. The compositional and structural changes associated with these processes can be analyzed using (scanning) transmission electron microscopy (S/TEM) with energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Vesicles formed in the space weathered rims of grains are thought to be filled with hydrogen or helium from the solar wind, although heating may be required for the formation of the vesicles. Solar wind hydrogen has been identified in vesicles in the space weathered rim of a pyroxene grain [1], while helium was suggested as the likely source of bubbles formed in a pyrrhotite grain [2].

Stratospheric IDPs from collection plate U2012, flown on NASA Ames Research Center U2 aircraft in March 1993, were washed and embedded in epoxy, then microtomed and placed on grids for STEM analysis. The samples were baked at 140°C for six hours to drive off adsorbed water before insertion in the UHV system. Electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS) data were collected with the NION UltraSTEM200-X at the U.S. Naval Research Laboratory, equipped with a Gatan Enfinium ER EEL spectrometer and a Bruker SSD-EDS detector. The STEM was operated at 60 kV or 200 kV, with a ~0.1 nm probe. Spectra were collected as spectrum images (SI), with a spectrum collected for each pixel, allowing for mapping of variations in thickness and composition.

Sample U2012A-2J contains a pyrrhotite grain with a nominally continuous space weathered rim full of subhedral to euhedral vesicles. The voids range in size from a few nanometers to ~30 nm. Brownlee et al. [2] suggested that these voids formed due to helium implantation, but were unable to confirm the presence of helium in specific voids. High resolution EELS mapping of several of the voids reveals a small peak at ~22 eV associated with individual voids, indicating they are filled with helium from the solar wind (Figure 1).

A vesicular grain observed in sample U2012A-3C is much more enigmatic (Figure 2). The core of the grain is iron sulfide and it is surrounded by a highly vesicular oxygen-rich shell. EDS data show the rim material contains significant O, Fe and S, along with several at% Mg and trace (~0.5 at%) Si. EELS data from the vesicles show small peaks at 8.5 eV and ~13 eV, both associated with hydrogen [1]. Additionally, the carbon K-edge in spectra from the same vesicles shows a distinct peak at 287.4 eV due to the presence of C-H bonds. Attribution of this peak to a specific compound is ambiguous due to the ubiquity of these types of bonds in natural materials as well as laboratory sources. The peak is associated only with this particle and clearly tied to the individual vesicles, suggesting it is indigenous. A sharp peak at the same energy is seen in hexamethyl disiloxane [3], a compound related to the silicone oil in which the IDPs were collected, and hexane [4], used to wash the IDPs, both possible sources of contamination. However, the vesicles are not correlated with significant Si, as expected for silicone oil, and evidence of contamination is not seen elsewhere on the sample. Isotope measurements of the grain are planned in order to clarify the possible sources of the rim material and hydrocarbons.

The helium- and hydrogen-filled bubbles have very different morphologies, and it is unlikely the hydrogen filled vesicles formed solely due to the influence of the solar wind. The cores of both grains are predominantly iron sulfide. However, while the helium vesicles are euhedral and in material that otherwise very closely resembles vesicle-free portions of the grain, the hydrogen vesicles are in a highly porous rim that is rich in oxygen relative to the core of the grain and also has other minor and trace elements (e.g., Mg, Si) not present in the core. Solar wind helium-filled vesicles in lunar ilmenite are not euhedral [5], indicating that both host mineral composition and heating could play a role in vesicle formation and shape.

With the ability to identify and map the volatile contents of very small vesicles in IDPs and other extraterrestrial materials, we can better understand the timing of alteration and source of volatiles, whether from atmospheric heating and decomposition of

pyllosilicates, implantation by the solar wind, or contamination during collection and laboratory preparation procedures. This technique is applicable to samples collected from many airless bodies including Itokawa, Bennu, and Ryugu.
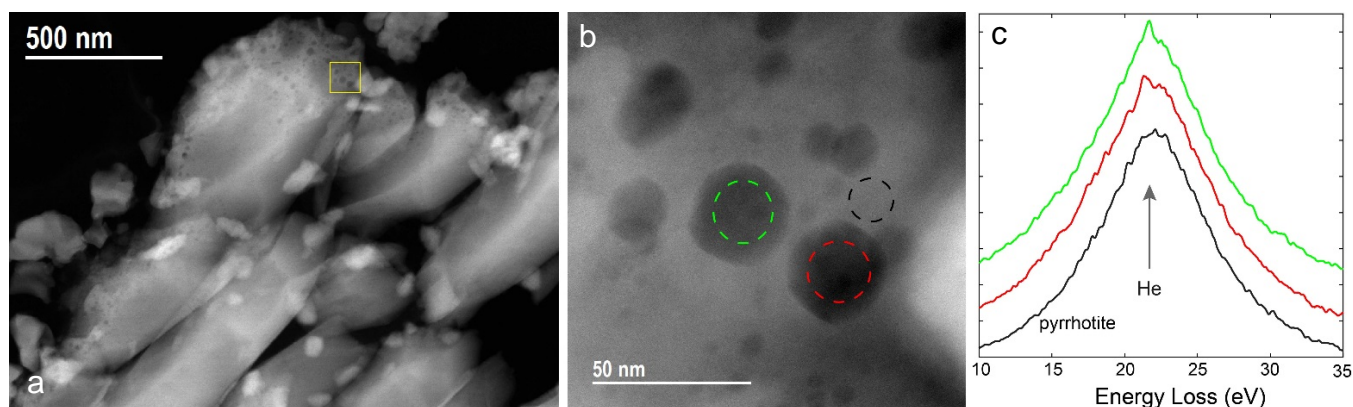

Figure 1. (a) HAADF image of pyrrhotite from U2012A-2J showing vesicle-rich rim around particle. (b) Higher magnification image of several euhedral vesicles. (c) EELS data from two vesicles indicated in (b) showing small peaks at ~22 eV indicating helium is present in the vesicles. A spectrum from a portion of the pyrrhotite not in a vesicle is shown for comparison (black).
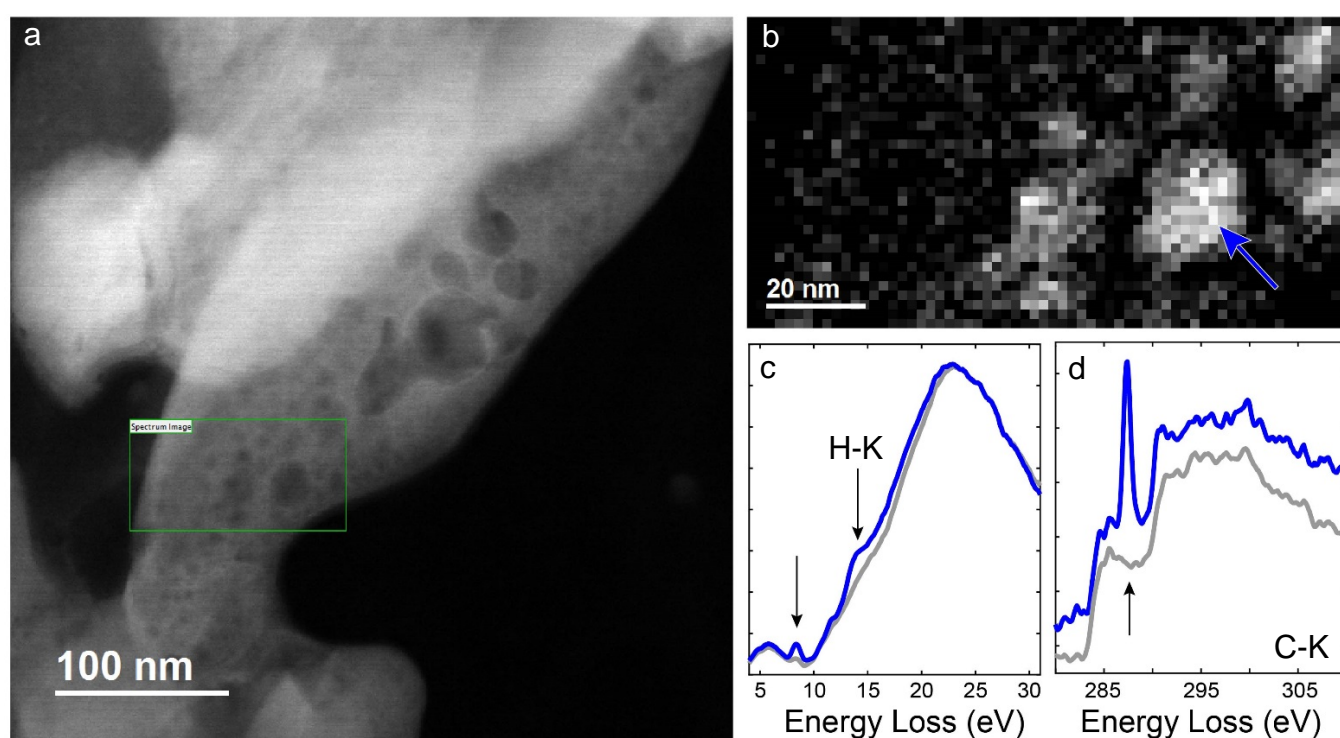

Figure 2. (a) HAADF image of particle in U2012A-3C with a vesicular rim. (b) Window map of 8.5 eV peak from region outlined by green box in (a). (c) Low loss spectra from the bright vesicle highlighted in (b) (blue) and surrounding material (gray) showing peaks at ~8.5 eV and ~13 eV, indicating the presence of hydrogen in the vesicles. (d) Carbon K-edge spectrum showing a large peak at 287.4 eV spatially associated with H-filled vesicles. The peak is indicative of C-H bonds. Amorphous carbon spectrum from the grid substrate (gray) is shown for comparison.

References
[1] Bradley, J.P., et al. (2014) *PNAS*, *111*, 1732. [2] Brownlee, D., et al. (1998) *LPSC*, *29*, Abstract #1869. [3] Urquhart, S.G., et al. (1997) *Organometallics*, *16*, 2080. [4] Hitchcock, A.P., and I. Ishii (1987) *Journal of Electron Spectroscopy and Related Phenomena*, *42*, 11. [5] Burgess, K. and R. Stroud (2017) *LPSC, 48*, Abstract # 1076.